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SYNTHESIS AND REACTIVITY OF SOME P-MESITYL SUBSTITUTED  
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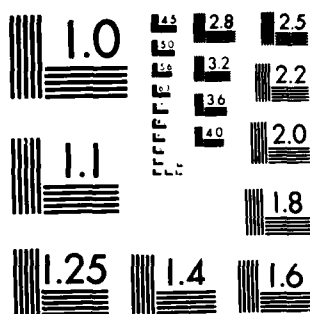
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Synthesis and Reactivity of Some P-Mesityl-

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by

Ze-min Xie and Robert H. Neilson

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  <p>The preparation and characterization of a series of P-mesityl substituted phosphorus compounds containing the Si-N-P and/or Si-C-P linkages are described. The reaction of <math>\text{RPCl}_2</math> (<math>R = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2</math>) with one equivalent of <math>(\text{Me}_3\text{Si})_2\text{NLi}</math> affords the thermally unstable chlorophosphine <math>(\text{Me}_3\text{Si})_2\text{NP(R)Cl}</math></p>		

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(1) in nearly quantitative yield. Substitution reactions of 1 are used to prepare the stable derivatives  $(\text{Me}_3\text{Si})_2\text{NP(R)X}$  (2,  $\text{X} = \text{Me}$ ; 3,  $\text{X} = \text{H}$ ; 4,  $\text{X} = \text{CH}_2\text{SiMe}_3$ ), while treatment with  $\text{Me}_3\text{SiN}_3$  yields the unstable azidophosphine  $(\text{Me}_3\text{Si})_2\text{NP(R)N}_3$  (5). The methylphosphine 2 reacts smoothly with  $\text{CCl}_4$  via elimination of  $\text{CHCl}_3$  with a [1,3]-silyl shift to form the chlorophosphinimine  $\text{Me}_3\text{SiN}=\text{P(R)}(\text{CH}_2\text{SiMe}_3)\text{Cl}$  (6), which is readily converted to the P-Me analogue 7 by reaction with  $\text{MeLi}$ . Depending on the reaction stoichiometry, treatment of  $\text{RPCl}_2$  with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  gives either the chlorophosphine  $\text{Me}_3\text{SiCH}_2\text{P(R)Cl}$  (8) as an unstable product from which 4 is produced by reaction with  $(\text{Me}_3\text{Si})_2\text{NLi}$ , or the stable disubstituted phosphine  $(\text{Me}_3\text{SiCH}_2)_2\text{PR}$  (9). Decomposition of the azidophosphine 5 proceeds with elimination of nitrogen and formation of the dimeric forms of the di(imino)phosphorane  $\text{RP}=\text{N}(\text{SiMe}_3)_2$  (5a). Either the cis (10) or trans (11) four-membered ring dimer can be isolated under appropriate conditions. Proton,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR data are reported for the new compounds.

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Synthesis and Reactivity of Some  
P-Mesityl Substituted Phosphorus Compounds

ZE-MIN XIE AND ROBERT H. NEILSON\*

Abstract

The preparation and characterization of a series of P-mesityl substituted phosphorus compounds containing the Si-N-P and/or Si-C-P linkages are described. The reaction of  $\text{RPCl}_2$  ( $\text{R} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) with one equivalent of  $(\text{Me}_3\text{Si})_2\text{NLi}$  affords the thermally unstable chlorophosphine  $(\text{Me}_3\text{Si})_2\text{NP}(\text{R})\text{Cl}$  (1) in nearly quantitative yield. Substitution reactions of 1 are used to prepare the stable derivatives  $(\text{Me}_3\text{Si})_2\text{NP}(\text{R})\text{X}$  (2,  $\text{X} = \text{Me}$ ; 3,  $\text{X} = \text{H}$ ; 4,  $\text{X} = \text{CH}_2\text{SiMe}_3$ ), while treatment with  $\text{Me}_3\text{SiN}_3$  yields the unstable azidophosphine  $(\text{Me}_3\text{Si})_2\text{NP}(\text{R})\text{N}_3$  (5). The methylphosphine 2 reacts smoothly with  $\text{CCl}_4$  via elimination of  $\text{CHCl}_3$  and a [1,3]-silyl shift to form the chlorophosphinimine  $\text{Me}_3\text{SiN}=\text{P}(\text{R})(\text{CH}_2\text{SiMe}_3)\text{Cl}$  (6), which is readily converted to the P-Me analogue 7 by reaction with  $\text{MeLi}$ . Depending on the reaction stoichiometry, treatment of  $\text{RPCl}_2$  with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  gives either the chlorophosphine  $\text{Me}_3\text{SiCH}_2\text{P}(\text{R})\text{Cl}$  (8) as an unstable product from which 4 is produced by reaction with  $(\text{Me}_3\text{Si})_2\text{NLi}$ , or the stable disubstituted phosphine  $(\text{Me}_3\text{SiCH}_2)_2\text{PR}$  (9). Decomposition of the azidophosphine 5 proceeds with elimination of nitrogen and formation of the dimeric forms of the di(imino)phosphorane  $\text{RP}=\text{NSiMe}_3)_2$  (5a). Either the cis (10) or trans (11) four-membered ring dimer can be isolated under appropriate conditions. Proton,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR data are reported for the new compounds.

## Introduction

Currently, there is considerable interest in the chemistry of "low-coordinate" phosphorus compounds such as the 2-coordinate phosphines<sup>1</sup>  $R-P=E$  and the 3-coordinate phosphoranes<sup>2</sup>  $R-P(=E)_2$  where  $E = NR'$  or  $CR'_2$ . Several examples of stable compounds of each type now exist and some reports of their derivative chemistry<sup>3</sup> have appeared recently. Our interest in such compounds stems mainly from the possibility that they might be useful precursors to new classes of phosphorus-containing polymers or cyclic oligomers. It seems reasonable that systems suited to this purpose should contain: (1) a sterically bulky, unreactive group on phosphorus to provide kinetic stability, and (2) functional linkages such as Si-N-P and/or Si-C-P which could serve as sites for condensation-polymerization reactions.<sup>4,5</sup>

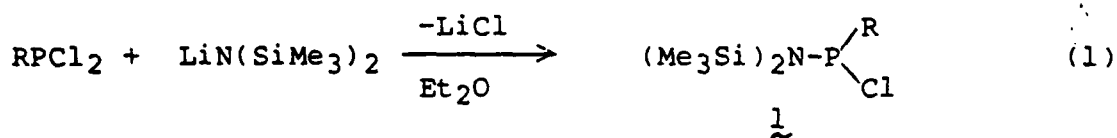
As the initial phase of this project, we report here on the synthesis and reactivity of a series of silylated, P-mesityl substituted compounds. The potential uses of some of these reagents in the preparation of low-coordinate species and new oligomers will be described in subsequent papers.

## Results and Discussion

Mesityldichlorophosphine  $RPCl_2$  ( $R = 2,4,6-Me_3C_6H_2$ ) was selected as the starting material in this study for essentially two reasons: (1) it provides an unreactive P-C bond with a substantial amount of steric hinderance around phosphorus, and (2) it is easily prepared in relatively large quantity (~100g) and good yield (~80%) from  $PCl_3$  and mesityl Grignard reagent.

The reactions described herein were primarily intended to introduce Si-N-P or Si-C-P linkages in various arrangements for the purpose outlined above.

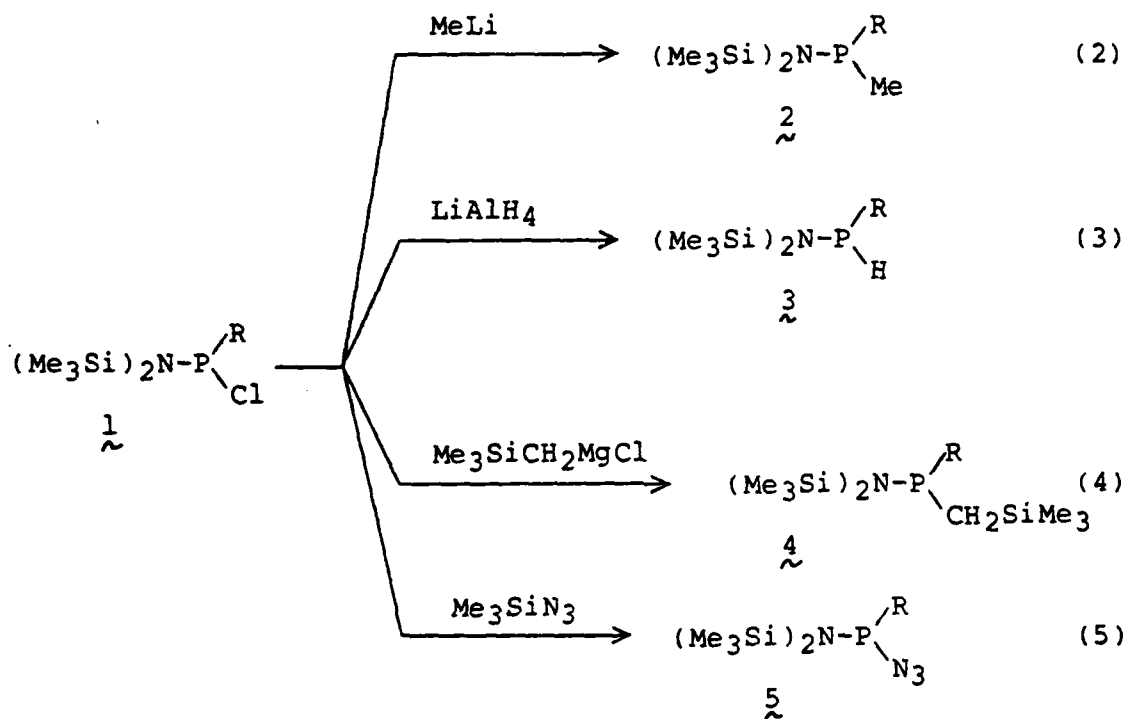
Treatment of  $\text{RPCl}_2$  ( $\text{R} = \text{mesityl}$ ) with one equivalent of lithium bis(trimethylsilyl)amide (eq 1) in ether solution gave the important reagent, [bis(trimethylsilyl)amino](chloro)-(mesityl)phosphine (1). Compound 1 was obtained in ca. 90% yield



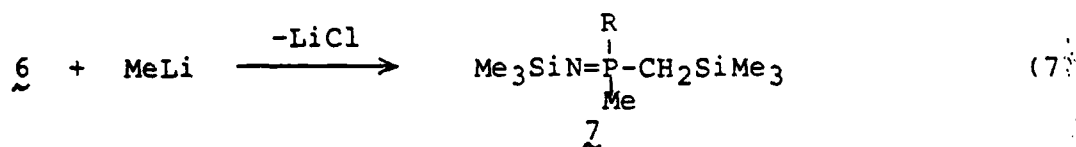
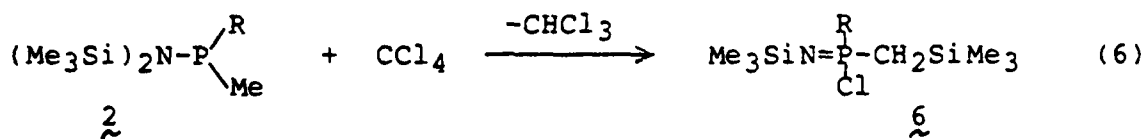
as a viscous orange-brown liquid which was characterized by NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) spectroscopy (Table I) and by its derivative chemistry. Even when traces of  $\text{LiCl}$  were tediously removed from 1, however, it could not be distilled without substantial thermal decomposition to  $\text{Me}_3\text{SiCl}$  and a complex mixture of unidentified non-volatile products. Undistilled samples of 1, nevertheless, were of sufficient purity to provide good NMR spectra and to be used in subsequent reactions.

The chlorophosphine 1 reacted smoothly with  $\text{MeLi}$  (eq 2),  $\text{LiAlH}_4$  (eq 3), and  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (eq 4) to yield the distillable liquid products 2, 3, and 4, respectively. These derivatives were characterized by elemental analysis (Table II) in addition

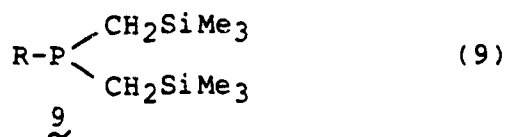
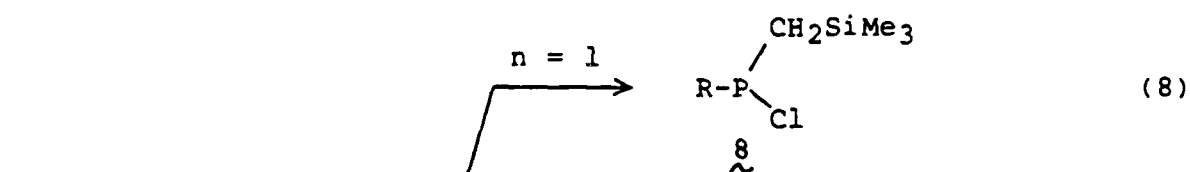
to NMR spectroscopy. The azidophosphine 5 was obtained as an unstable species (see below) from the slow, but eventually quantitative reaction of 1 with trimethylsilyl azide (eq 5).



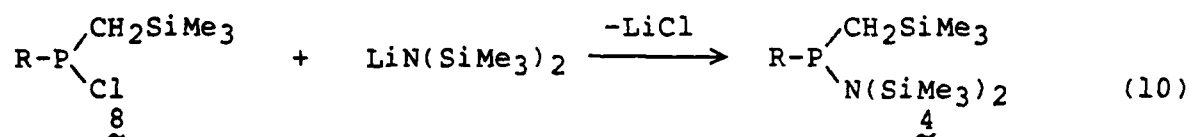
In addition to providing chemical confirmation of the P-Cl reagent 1, derivatives 2-5 are synthetically useful compounds themselves. For example, the CCl<sub>4</sub> reaction (eq 6) of the P-methyl phosphine 2 proceeded with elimination of CHCl<sub>3</sub> and silyl group migration from nitrogen to carbon<sup>6,7</sup> affording the P-chlorophosphinimine 6 in high yield. Compound 6 gave the P-methyl analogue 7 upon treatment with MeLi (eq 7).



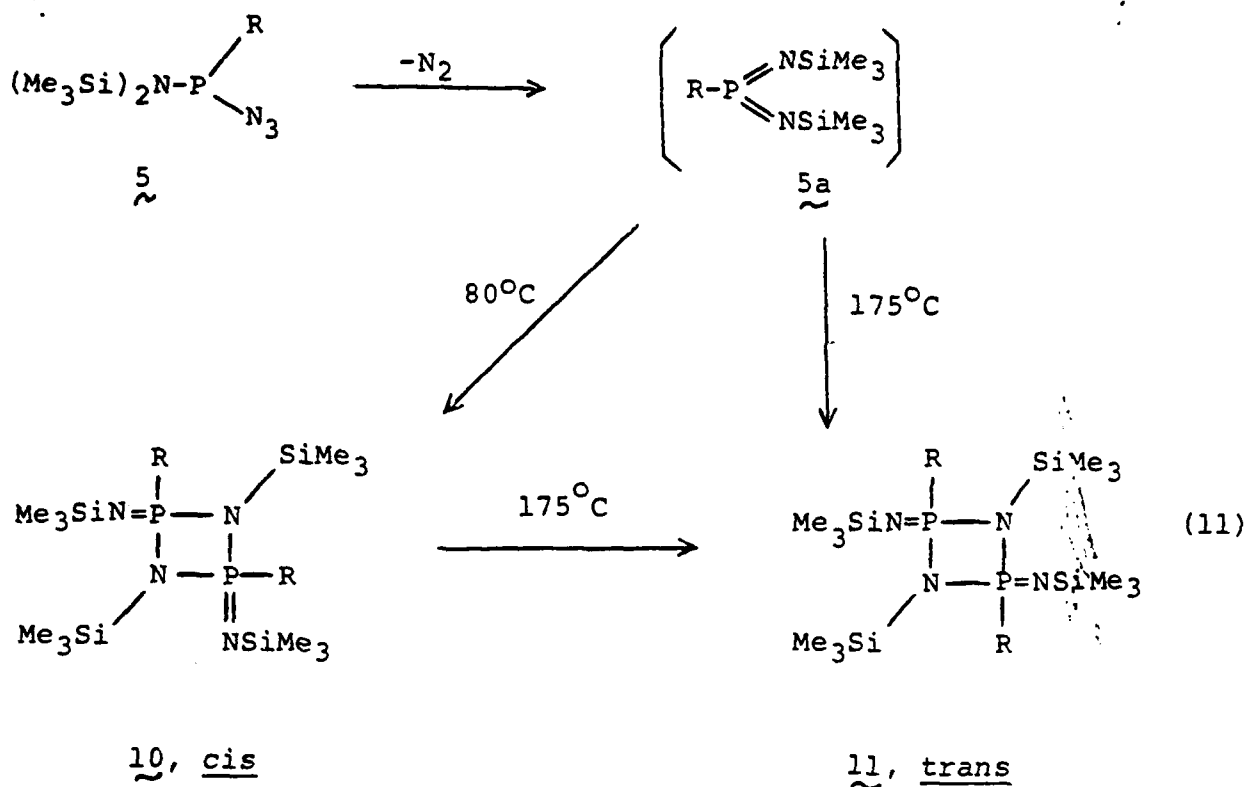
As part of this study, we were also interested in preparing P-mesityl systems containing the Si-C-P linkage alone (i.e. without silylamino substituents). The reaction of  $\text{RPCl}_2$  with one equivalent of the (trimethylsilyl)methyl Grignard reagent (eq 8) was, unfortunately, not entirely successful in that regard. The desired monochlorophosphine  $\underset{\sim}{8}$  was obtained but only as an impure product which could not be distilled without extensive decomposition. Its characterization is therefore based on  $^1\text{H}$



and  $^{31}\text{P}$  NMR data; a satisfactory  $^{13}\text{C}$  spectrum was not obtained due to its insufficient purity and ease of decomposition. The NMR spectra of the residue after  $\text{Me}_3\text{SiCl}$  elimination indicate the formation of  $\text{P}-\text{CH}_2-\text{P}$  condensation products but no specific compounds could be identified. The use of excess Grignard reagent (eq 9) did allow the preparation of the disubstituted product 9 as a well-characterized, thermally stable derivative. Compound 9 was, in fact, usually observed as a hard-to-separate impurity in the preparation of 8. Additional chemical evidence for the chlorophosphine 8 was found in its reaction with  $\text{LiN}(\text{SiMe}_3)_2$  which gave 4 in about 50% yield (eq 10).



As mentioned above, the azidophosphine 5 was thermally unstable, decomposing with loss of  $\text{N}_2$  even at room temperature. Its thermolysis was studied under a variety of conditions in an effort to isolate the likely decomposition product, bis(trimethylsilylimino)(mesityl)phosphorane 5a. Although the 3-coordinate phosphorane 5a could not be directly observed, its

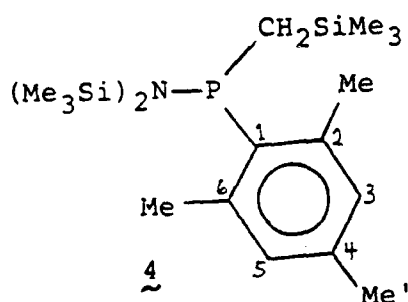


dimerization products 10 and 11 were each obtained as pure crystalline solids (eq 11). When 5 was heated either in refluxing  $\text{CH}_2\text{Cl}_2$  or neat at  $80^\circ\text{C}$ , the cis isomer 10 was formed. Decomposition under more vigorous conditions (neat,  $175^\circ\text{C}$ ) gave the trans isomer 11 which was also produced when 10 was heated at the same temperature. The dimers were characterized by elemental analysis, NMR spectroscopy and molecular weight measurements (by mass spectroscopy and cryoscopically in benzene). The structures of the isomers are assigned on the basis of their relative formation temperatures, melting points, and  $^{31}\text{P}$  chemical shifts.<sup>1c</sup>

One of the main goals of this study was to compare the thermal stability and chemical reactivity of the P-mesityl

compounds with the previously reported  $\text{P-N}(\text{SiMe}_3)_2$  systems. Several differences as well as some similarities are noteworthy. First, the chlorophosphines 1 and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{PCl}$  are both unstable with respect to elimination of  $\text{Me}_3\text{SiCl}$ . The mesityl compound 1 yields an uninterpretable mixture of phosphorus products, whereas, the latter gives the stable 2-coordinate phosphine  $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3$ .<sup>1i</sup> Second, the P-H derivatives 3 and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{PH}$  are both stable, distillable compounds as are a number of other recently prepared (silylamino)phosphines with P-H bonds.<sup>8-10</sup> Third, the chloro(trimethylsilylmethyl)phosphines 8 and  $(\text{Me}_3\text{Si})_2\text{NP}(\text{Cl})\text{CH}_2\text{SiMe}_3$  show different modes of reactivity toward bases such as  $\text{LiN}(\text{SiMe}_3)_2$ . While 8 yields the simple nucleophilic substitution product 4, the  $(\text{Me}_3\text{Si})_2\text{N-}$  derivative is dehydrohalogenated and the novel (methylene)phosphine  $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$  is obtained in high yield.<sup>1c</sup> Finally, the azidophosphines 5 and  $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{PN}_3$  both decompose with elimination of  $\text{N}_2$  and [1,3]-silyl migration but 5 affords only the dimers 10 and 11, whereas the stable monomeric phosphorane  $(\text{Me}_3\text{Si})_2\text{NP}=\text{NSiMe}_3)_2$  is obtained from the persilylated system.<sup>2e</sup> The formation of dimeric products from the decomposition of 5 is similar to the behavior of other compounds including  $(\text{Me}_3\text{Si})_2\text{NP}(\text{N}_3)\text{R}$  ( $\text{R} = \text{CH}_2\text{SiMe}_3$ <sup>1c</sup> and  $\text{Ph}$ <sup>11</sup>). Viewed in total, these results suggest that the mesityl group is somewhat less effective than  $(\text{Me}_3\text{Si})_2\text{N}$  in its ability to kinetically stabilize low-coordinate phosphorus compounds.

Finally, some features of the  $^{13}\text{C}$  NMR spectra of these P-mesityl compounds are worthy of note. Although compounds 1-11 all have chiral phosphorus centers, the planarity of the mesityl group renders the ortho methyl groups magnetically equivalent unless rotation about the P-C bond is restricted on the NMR time scale. Such hindered rotation was noted by Bickelhaupt<sup>12</sup> for the two-coordinate ( $\text{sp}^2$ ) phosphine  $\text{Mes-P=CPh}_2$ . However, with the exception of the sterically congested dimers 10 and 11, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data (Table I) reported here for the three-coordinate ( $\text{sp}^3$ ) phosphines are consistent with free rotation about the P-C bond. For example, the mesityl portions of the  $^{13}\text{C}$  NMR spectrum of 4 are completely assigned as follows. The observation of



	$\delta (^{13}\text{C})$	$J_{\text{PC}}$
Me	23.19	18.3
Me'	21.07	-
C <sub>1</sub>	137.26	42.0
C <sub>2,6</sub>	142.13	16.6
C <sub>3,5</sub>	130.53	-
C <sub>4</sub>	138.14	-

three peaks in the methyl region is interpreted as a doublet due to the equivalent ortho methyl groups with spin coupling to phosphorus, and a singlet due to the more remote para methyl substituent. When the  $^{13}\text{C}$  spectrum of 4 was recorded in different solvents, the splitting of 18.3 Hz remained constant, indicating that it is reasonably assigned as a coupling constant ( $^3J_{\text{PC}}$ ) rather than a chemical shift difference.

The magnitude of this  $^3J_{PC}$  (18.3 Hz) is well within the range of values obtained on related  $P^{III}$  systems.<sup>10,11</sup> The  $^{13}C$  spectra of the other compounds are similar, although, in some cases, overlap of the resonances for the ring carbons ( $C_1-C_6$ ) made individual peak assignments difficult. Consequently, only ranges of  $\delta$  values are listed for these carbons in Table I.

### Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: mesityl bromide,  $(Me_3Si)_2NH$ ,  $PCl_3$ ,  $Me_3SiCH_2Cl$ ,  $Me_3SiN_3$ ,  $n-BuLi$  (hexane solution), and ether solutions of  $MeLi$ ,  $MeMgBr$ , and  $LiAlH_4$ . Ether and THF were distilled from  $CaH_2$  prior to use; other solvents were dried over molecular sieves. The Grignard reagent  $Me_3SiCH_2MgCl$  was prepared according to the published procedure<sup>13</sup>. Mesityldichlorophosphine<sup>14</sup> was prepared in 85% yield from  $MesMgBr$ <sup>15</sup> and  $PCl_3$  by a procedure similar to that used by Clark<sup>16</sup> for the synthesis of  $(o-tolyl)_2PCl$ . Proton NMR spectra were recorded on a Varian EM-390 spectrometer;  $^{13}C$  and  $^{31}P$  NMR, both with  $^1H$  decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Mass spectral data were obtained on a Finnagin GC-MS system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

[Bis(trimethylsilyl)amino](chloro)(mesityl)phosphine (1). A solution of  $(\text{Me}_3\text{Si})_2\text{NLi}$ , prepared from  $(\text{Me}_3\text{Si})_2\text{NH}$  (7.5 mL, 36 mmol) and  $n\text{-BuLi}$  (20.6 mL, 1.7 M), in  $\text{Et}_2\text{O}$  (30 mL) was added at  $0^\circ\text{C}$  to a stirred solution of  $\text{MesPCl}_2$  (8.0 g, 36 mmol) in  $\text{Et}_2\text{O}$  (30 mL). The mixture was allowed to warm to room temperature and was stirred for 3 hours. Ether was removed under vacuum and hexane ( $\sim 60$  mL) was added to extract the product from the lithium salts. After stirring for 2 hours, the mixture was filtered under nitrogen and the filtrate was kept at  $-15^\circ\text{C}$  overnight. An additional small amount of solid was separated by decanting the solution and the solvent was removed from the decantate leaving 1 as an orange liquid (11.2 g, 90% yield, purity estimated to be  $\sim 95\%$  by  $^1\text{H}$  and  $^{31}\text{P}$  NMR). On attempted distillation, the compound decomposed rapidly above  $100^\circ\text{C}$  giving  $\text{Me}_3\text{SiCl}$  and unidentified non-volatile products.

[Bis(trimethylsilyl)amino](mesityl)(methyl)phosphine (2). Methyllithium (65 mL, 1.6 M) was added slowly at  $0^\circ\text{C}$  to a stirred solution of 1 (34g, 0.1 mol) prepared as above, in  $\text{Et}_2\text{O}$  (150 mL). After warming to room temperature and stirring for one hour  $\text{Et}_2\text{O}$  was removed and hexane (200 mL) was added. The mixture was filtered, allowed to stand at  $-15^\circ\text{C}$ , decanted, and freed of solvent. Compound 2 (Table II) was isolated as a colorless liquid by vacuum distillation.

[Bis(trimethylsilyl)amino](mesityl)phosphine (3). In the same manner, the chlorophosphine 1 (22.7 g, 66 mmol) in  $\text{Et}_2\text{O}$  (100 mL) was treated with  $\text{LiAlH}_4$  (18 mL, 1.0 M) at  $0^\circ\text{C}$ . After stirring overnight at room temperature, the mixture was filtered and the

solvent was removed under vacuum. Distillation gave the P-H derivative 3 (Table II) as a colorless liquid.

[Bis(trimethylsilyl)amino](mesityl)(trimethylsilylmethyl)-phosphine (4). From 1. A solution of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (ca. 100 mmol in 100 mL  $\text{Et}_2\text{O}$ ) was added at  $0^\circ\text{C}$  to a stirred solution of 1 (33.5g, 96 mmol) in  $\text{Et}_2\text{O}$  (100 mL). After stirring for 4 hours at room temperature, compound 4 (Table II) was obtained as a colorless liquid using the procedure described above for 2. From 8. The chlorophosphine 8 (22 g, 81 mmol), prepared as described below, was added at  $0^\circ\text{C}$  to a stirred solution of  $\text{LiN}(\text{SiMe}_3)_2$  (ca. 90 mmol, prepared from  $(\text{Me}_3\text{Si})_2\text{NH}$  and  $n\text{-BuLi}$ ) in THF (50 ml) at  $0^\circ\text{C}$ . The mixture was stirred overnight at room temperature. Filtration, solvent removal, and distillation gave 4 as a colorless liquid (16 g, 50% yield).

Azido[bis(trimethylsilyl)amino](mesityl)phosphine (5). A freshly prepared sample of 1 (5.0 g, 14.5 mmol) was treated with  $\text{Me}_3\text{SiN}_3$  (2.5g, 21.7 mmol) at  $0^\circ\text{C}$ . After stirring for 2 hours, the mixture was allowed to stand at  $-15^\circ\text{C}$  for 72 hours in order to complete the reaction with minimal decomposition of the azidophosphine product. The excess azidosilane and  $\text{Me}_3\text{SiCl}$  were removed under vacuum leaving compound 5 which was found to be of high purity by NMR spectroscopy. Attempted distillation caused elimination of  $\text{N}_2$  and dimerization as described below.

P-Chloro-P-mesityl-P-(trimethylsilylmethyl)-N-(trimethylsilyl)phoshinimine (6). The P-methylphosphine 2 (22.0 g, 67.6 mmol) was treated with  $\text{CCl}_4$  (13.8 mL, 143 mmol) at  $0^\circ\text{C}$ .

After stirring overnight at room temperature, distillation gave 6 as a colorless liquid (Table II).

P-Bis(trimethylsilyl)amino-P-mesityl-P-methyl-N-(trimethylsilyl)phosphinimine (7). Methylolithium (33 mL, 1.6M) was added at  $-40^{\circ}\text{C}$  to a stirred solution of the chlorophosphinimine 6 (18.0 g, 50 mmol) in  $\text{Et}_2\text{O}$  (50 mL). After stirring for 1 hour at  $-40^{\circ}\text{C}$ , the mixture was allowed to warm to room temperature with stirring overnight. Filtration, solvent removal, and distillation gave 7 as a colorless liquid (Table II).

Chloro(trimethylsilylmethyl)(mesityl)phosphine (8). A solution of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (ca. 100 mmol in 40 mL  $\text{Et}_2\text{O}$ ) was added at  $-78^{\circ}\text{C}$  over 30 min to a stirred solution of  $\text{MesPCl}_2$  (22.5 g, 100 mmol) in  $\text{Et}_2\text{O}$  (50 mL). After stirring overnight at room temperature, the  $\text{Et}_2\text{O}$  was removed and hexane (150 mL) was added. The mixture was then filtered and the filtrate was allowed to stand at  $-15^{\circ}\text{C}$  overnight, during which time some additional solids were precipitated. The supernatant liquid was decanted and solvent removal gave 8 as an orange liquid (22 g, ca. 80% yield) which was 85-90% pure as indicated by  $^1\text{H}$  and  $^{31}\text{P}$  NMR (Table I). The compound evolved  $\text{Me}_3\text{SiCl}$  slowly on standing at room temperature or rapidly on attempted distillation to yield unidentified non-volatile products.

Bis(trimethylsilylmethyl)(mesityl)phosphine (9). In a similar manner,  $\text{MesPCl}_2$  (18.8 g, 85 mmol) in  $\text{Et}_2\text{O}$  (80 mL) was treated at  $0^{\circ}\text{C}$  with  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (ca. 200 mmol in 80 mL  $\text{Et}_2\text{O}$ ). The same work-up procedure as described for 8 afforded compound 9.

as a stable, colorless liquid after vacuum distillation (Table II).

Preparation of the dimers (10 and 11) of Bis(trimethylsilylimino)(mesityl)phosphorane (5a). A freshly prepared sample of the azidophosphine 5 (5.0 g, 14.4 mmol) was heated without a solvent at 80°-85°C for 30 minutes. Gas evolution and formation of yellow solid was observed. Slow crystallization from hexane (5 mL) at -15°C gave white crystals of the cis dimer 10 (2.27 g, 50% yield, mp 171°C). When the decomposition of 5 was conducted in refluxing CH<sub>2</sub>Cl<sub>2</sub> solution and monitored by <sup>1</sup>H and <sup>31</sup>P NMR, 10 was the only observable product; no evidence of the monomer 5a was obtained. The trans isomer 11 (mp 230°C) was prepared in 42% yield by heating a neat sample of 10 at 175°C for 1 hour, followed by recrystallization from hexane at -15°C. Alternatively, the trans dimer 11 was obtained directly from the rapid decomposition of the azidophosphine 5 at 175°C. Mass spectra of both 10 and 11 contained a significant parent ion peak at m/e 648 and a large peak corresponding to the monomer 5a. Major fragments in mass spectrum of 10, m/e (relative intensity) = 648 (2), 633 (5), 325 (11), 324 (4), 310 (12), 309 (47), 146 (13), 130 (21), 74 (22), 73 (100), 45 (20). Molecular weights were also determined by freezing point depression measurements in benzene solution: 10, 638; 11, 586 (calcd 648).

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## References and Notes

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Table I. . NMR Spectroscopic Data<sup>a</sup>

Compd (R = Mesityl)	Signal	<sup>1</sup> H NMR		<sup>13</sup> C NMR		<sup>31</sup> P NMR
		δ	J <sub>PH</sub>	δ	J <sub>PC</sub>	δ
$\begin{array}{c} \text{(Me}_3\text{Si)}_2\text{N}-\text{P} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{Cl} \end{array} \\ \sim 1 \end{array}$	Me <sub>3</sub> Si	0.31	1.8	4.00	8.8	151.1
	o-Me	2.60	2.5	23.85	13.7	
	p-Me	2.28	1.8	20.99		
	C <sub>6</sub> H <sub>2</sub>	6.80	3.6	131- 141		
$\begin{array}{c} \text{(Me}_3\text{Si)}_2\text{N}-\text{P} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{Me} \end{array} \\ \sim 2 \end{array}$	Me <sub>3</sub> Si	0.24		4.15	6.8	47.8
	PMe	1.88	8.2	22.29	52.7	
	o-Me	2.52		22.74	15.6	
	p-Me	2.28		20.40		
	C <sub>6</sub> H <sub>2</sub>	6.74	2.7	130- 140		
$\begin{array}{c} \text{(Me}_3\text{Si)}_2\text{N}-\text{P} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{H} \end{array} \\ \sim 3 \end{array}$	Me <sub>3</sub> Si	0.21	1.2	3.15	6.9	-10.4
	PH	6.28	228.0			
	o-Me	2.40	2.3	22.68	5.9	
	p-Me	2.25	1.8	21.05		
	C <sub>6</sub> H <sub>2</sub>	6.75	2.4	129- 140		

Table I. continued

Compd (R = Mesityl)	Signal	1H NMR		13C NMR		31P NMR
		$\delta$	$J_{PH}$	$\delta$	$J_{PC}$	$\delta$
$  \begin{array}{c}  \text{(Me}_3\text{Si)}_2\text{N}-\text{P} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{CH}_2\text{SiMe}_3 \end{array} \\  \sim 4  \end{array}  $	(Me <sub>3</sub> Si) <sub>2</sub> N	0.21		5.13	5.9	50.9
	Me <sub>3</sub> SiC	0.01		0.16	4.9	
	PCH <sub>2</sub> <sup>b</sup>	1.81	8.7	22.87	42.7	
		2.29	1.2			
	o-Me	2.60		23.19	18.3	
	p-Me	2.23		21.07		
	C <sub>6</sub> H <sub>2</sub>	2.0		130- 142		
$  \begin{array}{c}  \text{(Me}_3\text{Si)}_2\text{N}-\text{P} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{N}_3 \end{array} \\  \sim 5  \end{array}  $	Me <sub>3</sub> Si	0.31	1.8	3.87	6.8	124.8
	o-Me	2.60	2.5	23.49	10.7	
	p-Me	2.28	2.2	20.86		
	C <sub>6</sub> H <sub>2</sub>	6.80	3.6	131- 141		
$  \begin{array}{c}  \text{Me}_3\text{SiN}=\text{P} \begin{array}{l} \nearrow \text{R} \\ \searrow \text{Cl} \\ \downarrow \text{CH}_2\text{SiMe}_3 \end{array} \\  \sim 6  \end{array}  $	Me <sub>3</sub> SiN	0.25		3.20	4.9	13.2
	Me <sub>3</sub> SiC	0.21		0.00	3.9	
	CH <sub>2</sub> <sup>b</sup>	2.01	26.5	33.75	69.3	
		2.29	7.9			
	o-Me	2.83	0.9	24.65	2.9	
	p-Me	2.35		20.98		
	C <sub>6</sub> H <sub>2</sub>	6.94	4.8	131- 142		

Table I. continued

Compd (R = Mesityl)	Signal	<sup>1</sup> H NMR		<sup>13</sup> C NMR		<sup>31</sup> P NMR
		δ	J <sub>PH</sub>	δ	J <sub>PC</sub>	δ
$\begin{array}{c} \text{Me}_3\text{SiN}=\text{P}-\text{Me} \\   \\ \text{R} \\   \\ \text{CH}_2\text{SiMe}_3 \end{array}$ <p>7</p>	Me <sub>3</sub> SiN	0.07		3.68	3.9	3.8
	Me <sub>3</sub> SiC	-0.04		0.13	1.1	
	PMe	1.84	12.6	26.02	75.2	
	CH <sub>2</sub> <sup>b</sup>	1.35	25.1	25.76	67.4	
		1.65	10.6			
	o-Me	2.63		24.17	6.1	
	p-Me	2.26		20.57		
	C <sub>6</sub> H <sub>2</sub>	6.81	3.3	131- 143		
$\begin{array}{c} \text{CH}_2\text{SiMe}_3 \\ / \\ \text{R}-\text{P} \\ \backslash \\ \text{Cl} \end{array}$ <p>8</p>	Me <sub>3</sub> Si	0.03				88.2
	CH <sub>2</sub>	2.32	13.8			
	o-Me	2.70	2.4			
	p-Me	2.28				
	C <sub>6</sub> H <sub>2</sub>	6.78	2.7			
$\begin{array}{c} \text{CH}_2\text{SiMe}_3 \\ / \\ \text{R}-\text{P} \\ \backslash \\ \text{CH}_2\text{SiMe}_3 \end{array}$ <p>9</p>	Me <sub>3</sub> Si	-0.06		-0.18	5.8	26.9
	CH <sub>2</sub> <sup>b</sup>	1.02	2.1	18.74	71.3	
		1.50	0.7			
	o-Me	2.60		23.27	21.5	
	p-Me	2.24		18.52		
	C <sub>6</sub> H <sub>2</sub>	6.76	1.8	129- 145		

Table I. continued

Compd (R = Mesityl)	signal	<sup>1</sup> H NMR		<sup>13</sup> C NMR		<sup>31</sup> P NMR
		δ	J <sub>PH</sub>	δ	J <sub>PC</sub>	δ
$  \begin{array}{c}  \text{NSiMe}_3 \\     \\  [\text{Me}_3\text{SiN}-\text{P}-\text{R}]_2 \\    \quad    \end{array}  $	Me <sub>3</sub> Si	0.07		3.31	4.3	-19.7
		0.43		3.51	5.5	
	o-Me	2.46		25.42	4.9	
				25.42	0.0	
	p-Me	2.18		20.95		
<u>10</u> , <u>cis</u>	C <sub>6</sub> H <sub>2</sub>	6.66	4.2	130- 140		
	Me <sub>3</sub> Si	-0.02		0.97		-24.7
		0.04		3.53		
	o-Me	2.86		26.19	0.0	
				26.21	5.5	
<u>11</u> , <u>trans</u>	p-Me	2.24		20.83		
	C <sub>6</sub> H <sub>2</sub>	6.86	4.2	131- 141		

a Chemical shifts downfield from Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C and from H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P spectra; coupling constants in Hz. Solvents: <sup>1</sup>H, CH<sub>2</sub>Cl<sub>2</sub>; <sup>13</sup>C and <sup>31</sup>P, CDCl<sub>3</sub>.

b Analysis of ABX pattern yields <sup>2</sup>J<sub>HH'</sub> values:

4, 13.5; 6, 14.4; 7, 14.7; 9, 13.8.

Table II. Preparative and Analytical Data

Compd	Preparative		Analytical <sup>a</sup>	
	% yield	bp, °C (mm)	%C	%H
<u>2</u>	68	106-108 (0.05)	59.60 (59.03)	10.30 (9.91)
<u>3</u>	63	98 (0.1)	58.00 (57.82)	9.46 (9.71)
<u>4</u>	62 (50) <sup>b</sup>	124-126 (0.04)	57.95 (57.37)	10.15 (10.14)
<u>6</u>	89	117-119 (0.03)	53.41 (53.39)	8.62 (8.69)
<u>7</u>	56	96-99 (0.03)	59.73 (60.12)	10.01 (10.09)
<u>8</u>	51	93-95 (0.03)	62.25 (62.91)	10.27 (10.25)
<u>10</u>	50	mp 170-171	54.49 (55.51)	8.93 (9.00)
<u>11</u>	42	mp 230	54.44 (55.51)	8.86 (9.00)

<sup>a</sup>Calculated values in parentheses. <sup>b</sup>Yield of 4 obtained by treatment of 8 with (Me<sub>3</sub>Si)<sub>2</sub>NLi (eq 10) is given in parentheses.